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(54) RESINOUS COATING COMPOSITION FORMING A HYGROSCOPIC NON-FOGGING COATING FILM WITH A HIGH SURFACE HARDNESS AND METHOD OF FORMING SUCH COATING FILMS

(71) We, NIPPON HYDRON CO., LTD., a corporation duly organised under the laws of Japan, of 8, 4-chome, Dosho-machi, Higashi-ku, Osaka-shi, Osaka-fu, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a resinous coating composition which forms a hygroscopic non-fogging coating film with a high surface hardness and to uses of such a composition.

It is considered desirable, and hitherto attempts have been made, to provide hygroscopic resinous coatings for the surfaces of window glass, windshields of automobile and aircraft, doors, mirrors, spectacle lenses, goggles, optical lenses and the like made of glass or transparent plastics to render them non-fogging.

However, the known hygroscopic resinous coating films do not possess sufficient surface hardness and, especially under high humidity, they absorb large quantities of moisture and swell to further decrease their surface hardness. This decrease in surface hardness allows them to become flawed when wiped by, e.g., hand or cloth to remove stains thereon and this results in an undesirable decrease in their commercial value. This susceptibility to scratching, can be mitigated by incorporating in the resinous coating a crosslinking agent to increase surface hardness to some extent, but incorporation of the crosslinking agent in an amount sufficient to increase the surface hardness to a satisfactory level causes a decrease in non-fogging property. It has been a

SPECIFICATION NO 1496345

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of NIPPON SHEET GLASS CO., LTD., a Corporation duly organised under the laws of Japan, of 8, 4-chome, Dosho-machi, Higashi-ku, Osaka, Japan, and National Patent Development Corporation, a Corporation duly organised under the laws of the State of Delaware, United States of America, of 375 Park Avenue, New York, N.Y. 10022, United States of America.

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inclusive of the atom on said resin at the reaction point.

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However, the known hygroscopic resinous coating films do not possess sufficient surface hardness and, especially under high humidity, they absorb large quantities of moisture and swell to further decrease their surface hardness. This decrease in surface hardness allows them to become flawed when wiped by, e.g., hand or cloth to remove stains thereon and this results in an undesirable decrease in their commercial value. This susceptibility to scratching, can be mitigated by incorporating in the resinous coating a crosslinking agent to increase surface hardness to some extent, but incorporation of the crosslinking agent in an amount sufficient to increase the surface hardness to a satisfactory level causes a decrease in non-fogging property. It has been a problem, therefore, to sufficiently enhance the surface hardness of the resinous coating without sacrificing the non-fogging characteristics.

In accordance with one aspect of the present invention, a resinous coating composition forming a hygroscopic non-fogging coating film having a high surface hardness is provided comprising a hydroscopic resin which is a polymer or co-polymer of at least one hydrophilic monomer chosen from hydroxy-lower alkyl acrylates, hydroxy-lower alkyl methacrylates, hydroxy-lower alkoxy lower alkyl acrylates and hydroxy-lower alkoxy lower alkyl methacrylates incorporated with (a) 5 to 60% by weight, based on the weight of the resin solid, of a surface active agent and (b) 5 to 70% by equivalent, based on the equivalent of the resin solid, of a crosslinking agent in which at least 80% of the functional groups are of the same kind, and having a single- or condensed-ring carbocyclic or heterocyclic skeleton, each ring being a 4- to 8-membered ring and the number of atoms forming the straight chain linkage between said ring and the reaction point with the resin of the crosslinking agent being at most 4 inclusive of the atom on said resin at the reaction point.

According to a further aspect of the invention there is provided a method of making a hygroscopic hydrophilic resinous article having a high surface hardness, which comprises:

a) moulding a hygroscopic resin to a desired shape; the resin being a polymer or copolymer of at least one hydrophilic monomer chosen from hydroxy-lower alkyl acrylates, hydroxy-lower alkyl methacrylates, hydroxy-lower alkoxy lower alkyl acrylates and hydroxy-lower alkoxy-lower alkyl methacrylates incorporated with (i) 5 to 60% by weight, based on resin solid of a surface active agent chosen from non-ionic surface active agents and possibly (ii) one component chosen from a catalyst and a cross linking agent as hereinbefore defined;

b) contacting the surface of the moulded article with a solution or vapour containing both, or the other of, the catalyst and cross-linking agent until it or they penetrate into the article and has or have a concentration therein gradually decreasing from the surface of the article towards the interior; at least the surface of the article resulting from operation (b) containing cross-linking agent in an amount of 5 to 70% equivalent based on the resin solid; and

c) then heat curing the article.

In this specification, including the claims, the term "lower" when applied to alkyl and alkoxy groups is intended to mean up to and including 4 carbon atoms.

A non-fogging coating film can be obtained by applying a resinous coating composition of the invention to a substrate and contacting the resulting coating film with water during, before and/or after a crosslinking step. The hardness of a coating film (hydrophilic resin layer) depends on its mechanical rigidity and may be enhanced by increasing the degree of crosslinking of the coating film, but the scratch resistance, i.e. strength determined by abrasion test by means of, e.g., gauze or cloth, is not determined by the mechanical rigidity alone. Namely, it is advantageous for scratch resistance that the coating film possesses a crosslinking density gradient in the direction of its thickness decreasing from the outer surface towards inside to impart a certain resiliency to the coating film itself, as in case of the coating film prepared in the method of the present invention as mentioned above. It is believed that a pressure imparted to the coating film is absorbed by the resiliency of the interior of the film and the net pressure imparted to the vicinity of the surface of the film is far smaller than the total pressure actually imposed, in this way the coating film may exhibit a remarkably higher scratch resistance than that predicted from the mechanical rigidity of the coating film itself. Thus, there is obtained an article having an enhanced surface hardness and an unexpectedly improved scratch resistance without any sacrifice in inherent hygroscopic and non-fogging properties of a hydrophilic hygroscopic resin by giving a crosslinking density gradient to the resin.

The present invention will now be further described with reference to the accompanying drawings in which;

Fig. 1 is a graph showing the relationship between the amount of a crosslinking agent incorporated and the surface hardness of a resinous coating film formed,

Fig. 2 is a cross-sectional view of an article coated with a composition in accordance with the present invention,

Figs. 3 to 5 are the cross-sectional views for illustrating the steps of a method of making hydrophilic hygroscopic articles in accordance with the present invention, and

Fig. 6 is a graph showing the relationship between the amount of a crosslinking agent incorporated and the non-fogging property of a coating film formed.

Examples of suitable hydrophilic acrylate and methacrylate polymers are:— polymers of 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, diethylene glycol monoacrylate, diethylene glycol monomethacrylate, triethylene glycol monoacrylate, triethylene glycol monomethacrylate, 2-hydroxy-propyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, dipropylene glycol monoacrylate and dipropylene glycol monomethacrylate.

The hygroscopic polymer may be modified, if necessary, by copolymerization with, e.g., acrylic acid, methacrylic acid, itaconic acid, fumaric acid or mono-2-hydroxypropyl itaconate.

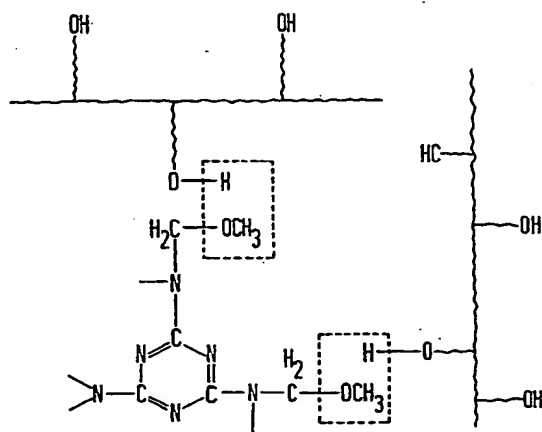
The aforesaid hydrophilic polymers may be used, if necessary, in solution in organic solvents, such as methanol, ethanol, isopropanol, ethylene glycol monomethyl ether, ethylene glycol monobutyl ether, dimethylformamide or dimethylsulfoxide.

Suitable crosslinking agents used are epoxy, melamine, amine and urea compounds including numerous compounds differing in number and kind of functional group, length of side chain and skeletal structure. Self-condensing reactions between functional groups in a crosslinking agent which should take part in crosslinking with a hygroscopic resin during crosslinking reaction step causes formation of plasticizer

compounds in a resinous coating film. The plasticizer compounds if formed by the self-condensing reaction retard absorption of moisture by the resin and impair its non-fogging property or reduce the hardness of the resins. Thus, the crosslinking agent should have a low tendency to self-condensation, in our compositions this is achieved by using cross-linking agents in which at least 80%, preferably at least 90% of functional groups are of the same kind.

It has been found that, among crosslinking agents having a linear or cyclic skeleton, those having cyclic skeletons provide a harder crosslinked resin; moreover, although there are compounds having a 3-membered ring or larger membered ring, those having a single- or condensed-ring carbocyclic or heterocyclic skeleton wherein each ring is a 4- to 8-membered ring have been found to give the best results. 3-membered ring compounds are considered unsuitable from a practical point of view because it is difficult to introduce therein functional groups in a sufficient number for crosslinking, while, on the other hand, the free deformation of the ring structure of 9- or larger-membered ring compounds reduces the extent to which cross-linking will suppress swelling of the resin upon absorption of moisture and prevent the coating film from becoming soft.

A coating film of a hygroscopic resin swells as it absorbs moisture, and the larger the degree of swelling of the coating film the softer the coating film becomes. It has been found, therefore, that the number of interatomic links which contribute to the swelling and flexibility of the coating film upon moisture absorption should be taken into consideration as a measure of the ease of swelling of the hygroscopic resin after reaction with a crosslinking agent. For instance, as shown in the following equation, on crosslinking reaction of poly(2-hydroxyethyl methacrylate) by means of hexamethoxymethylol melamine, there occurs a reaction between the functional groups ($-\text{OH}$) contained in the side chains of the polymer and the functional groups ($-\text{CH}_2-\text{O}-\text{CH}_3$) contained in the crosslinking agent to form $-\text{C}-\text{O}-$ linkages therebetween. As a result of the reaction taking place on many sides of molecular chains of the polymer, the polymer chains form a reticular structure through the crosslinking agent to form a tough coating film. Thus, the number of atoms linking the cyclic nucleus of the crosslinking agent to the hydrophilic functional group in the hygroscopic resin varies depending on the length of the side chain of the crosslinking agent, and this has an influence on the susceptibility to swell and, consequently, the hardness of the coating film. Therefore, the tendency of the coating film to swell on moisture absorption can be minimized by reducing the number of atoms linking the crosslinking agent nucleus and the polymer chain as far as possible to reduce the stretchability of the linkage.



The crosslinking agent should be selected on the basis of the above information and employed in the following amounts. The functional groups contained in a crosslinking agent react with the functional groups contained in a hygroscopic resin, such as $-\text{OH}$ groups. Therefore, we designate the amount of a cross-linking agent used in terms of the percentage of the chemical equivalent number of the functional groups contained in the crosslinking agent to the chemical equivalent number determined by the total number of the functional groups contained in monomers integrating said resin and capable of reacting with said crosslinking agent, rather than in

terms of the weight ratio of the crosslinking agent to the resin solid. For instance in the case of poly(2-hydroxyethyl methacrylate) as a hygroscopic resin, the polymer consists of several hundred to several thousand polymerized molecules of 2-hydroxyethyl methacrylate monomer and the monomer has one functional group ($-\text{OH}$) per molecule. Accordingly, one gram molecular weight, 130 g, of the monomer is regarded as a gram equivalent weight of the polymer, while, on the other hand, a gram equivalent weight of a crosslinking agent employed is calculated by dividing its gram molecular weight by the number of functional groups per molecule, and the amount of a crosslinking agent used would be indicated by a % by equivalent to the hygroscopic resin. That is to say, when the amount of a crosslinking agent used is 10% by equivalent, 10% of the functional groups contained in the hygroscopic resin, i.e. $-\text{OH}$ groups, will disappear through the crosslinking reaction subject to all the functional groups contained in the crosslinking agent taking part in crosslinking. On this occasion, theoretically it is presumed that the hygroscopicity of the resin decreases by 10%, though the hygroscopicity decreases, in practice, to a greater extent because of the decrease in rate of moisture absorption and the influence of filler. Accordingly it is essential not only to select an appropriate crosslinking agent but also to use a crosslinking agent in an adequate amount. We have found that no increase in hardness will be obtained when a crosslinking agent is used in a too small amount, while when used in too large an amount the hardness is increased but the hygroscopicity is impaired.

Because of its high wetting property a surface active agent incorporated in the coating film exerts a function of quickly transporting water from the surface of the film to functional groups which serve as moisture absorbing sites in the coating film. The surface active agent also should be incorporated in a controlled amount as set forth hereinafter since a slight amount of the surface active agent exerts no function as a moisture transporter and when used in a too large amount it hinders crosslinking reaction or deteriorates adhesion between the coating film and substrate.

Although there are many types of crosslinking agents, such as melamine derivatives, epoxides, amines and numerous others, for instance in the case of partially methylated hexamethylolmelamine as solid under the trade name "Uformite", an average of approximately 3.6 functional groups are methylated but the remaining 2.4 functional groups are in the form of $-\text{OH}$, $-\text{COOH}$ or $-\text{CHO}$, and therefore there occurs self-condensation of the crosslinking agent when a hygroscopic resin is crosslinked by means of the "Uformite"; as a result, the hygroscopicity of the resin is reduced to a great extent and, in addition, the hardness of the resin is not so enhanced as expected. On the contrary, in the case of hexamethoxymethylolmelamine (for example, sold under the trade name "Sumimal M-100") in spite of it being a melamine derivative, since all of its 6 functional groups are of the same $-\text{OCH}_3$ form little self-condensation occurs on crosslinking and, as a result, the hygroscopicity of the resin decreases proportionally to the amount of crosslinking agent and, conversely, the hardness increases.

With respect to the structure of crosslinking agent, it has been found that, for instance among crosslinking agents having 3 carboxyl groups per molecule, e.g., comparing trimellitic acid having a cyclic structure and citric acid having a linear structure, these carboxylic acids which have a cyclic structure are superior in enhancing hardness of coating film. Moreover, even with crosslinking agents having the same basic cyclic structure, comparing e.g. pyromellitic anhydride and hexamethoxymethylolmelamine, after undergoing a crosslinking reaction with functional groups on the side chains of a hygroscopic resin molecule, there are two atoms, oxygen and carbon, between the reaction point and the ring in case of the former while there are 3 atoms, oxygen, carbon and nitrogen, between the reaction point and the ring in case of the latter. The two crosslinking agents thus form different crosslinked structures; the pyromellitic anhydride needs a somewhat higher temperature but the achievable hardness of coating film is higher than when using hexamethoxymethylolmelamine in which the number of atoms lying between the reaction point and ring is less.

The relationship between the amount of crosslinking agent and the hardness of coating film is illustrated in detail in Fig. 1, which shows the relationship between the amount of a crosslinking agent and the hardness of a coating film obtained from a resin composition containing 2-hydroxyethyl methacrylate as a hygroscopic resin prepolymer; hexamethoxymethylolmelamine as a crosslinking agent; and 15 g equivalent, based on the equivalent weight of the crosslinking agent, of trifluoroacetic acid as a catalyst; the composition was arrived to a sheet glass as a film and cured at 110°C for 30 minutes.

The surface hardness is determined by the following abrasion test.

Abrasion test

A chip is prepared by cutting a commercially available cotton handkerchief and doubling it. A test piece is fixed on to a rotary table and, after sufficiently moistening the specimen of a coating film by expiration, the chip is placed on the test piece, and a load of 2 Kg/cm² applied thereto. The rotary table is then rotated by means of a driving motor at 120 r.p.m. The specimen is removed from the turn table at regular intervals for inspection and refixed on the table after application of sufficient moisture, again by expiration. This procedure is continued until noticeable scratches are formed on the surface of the specimen and the rotation time until the scratches are formed is taken as the index of surface hardness.

As is indicated by Fig. 1, we have found generally that the hardness begins to rapidly increase when the amount of crosslinking agent added amount to about 10% equivalent based on the equivalent weight of the hygroscopic resin solid and reaches the saturated value after the addition of approximately 60% equivalent. In many experiments on other crosslinking agents with varying structure and number of atoms contained in a stretchable linkage, in all cases, we have observed that the hardness increased suddenly when the amount of added crosslinking agent was in the region of 5 to 20% equivalent and that it exerted a saturated value when added in the amount of 50 to 70% equivalent. Thus, the amount of crosslinking agent to be incorporated in accordance with the present invention ranges from 5 to 70, preferably 15 to 40% equivalent.

Based on the many experimental results as shown in Fig. 1, the amount of a surface active agent which should be used to obtain satisfactory hygroscopic and non-fogging properties has been found to be 5 to 60, preferably 15 to 40% by weight based on the weight of hygroscopic resin solid. For instance, specimens of coating films were prepared in the same composition and curing conditions as shown in Fig. 1 using the crosslinking agent in an amount of 20% equivalent and a poly(oxyethylene) alkylphenyl ether-type nonionic surface active agent (Emulgen 903) in an amount of 3 or 20% by weight. When the specimens were stored for 30 minutes in a refrigerator maintained at -10°C and then left in a room of R.H. 60%, the surface fog disappeared in 10 minutes in the case of a specimen containing the surface active agent in an amount of 3% by weight while it disappeared within 1 minute in the case of a specimen containing it in an amount of 20% by weight. This indicates that the surface active agent incorporated in the resin assists migration of moisture absorbed within the resinous coating film to enhance the substantial hygroscopic and non-fogging properties of the film.

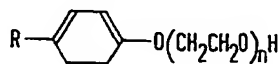
Suitable crosslinking agents for use in the present are for example those having the following single- or condensed-ring skeletal structures; benzene, naphthalene, triazine, pyridine, quinoline, isoquinoline, imidazole or like ring, which may contain, other than carbon atoms, oxygen, phosphorus, sulfur, nitrogen or other atoms, and bears a plurality of functional groups directly or indirectly bonded thereto, and having a low self-condensing property and forming, on crosslinking reaction, linkages between the cyclic skeleton and the functional group on the resin of said linkage containing at most 4 atoms including the atom of the reaction point between the skeleton and the reaction point.

Particular examples of the crosslinking agents are; phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, dimethylphthalic acid, dimethylterephthalic acid, naphthalic acid, naphthalenetetracarboxylic acid, dimethoxyquinone, perathol, camphoric acid, ceridonic acid, anhydromethylene citric acid, cinchomeronic acid, isocinchomeronic acid, pyrazinedicarboxylic acid, quinolinic acid, limethine, mechonine, coridardine, coridine, eryphthone, hexaalkoxymethylolmelamines, e.g. hexamethoxymethylolmelamine, hexaethoxymethylolmelamine and hexabutoxymethylolmelamine; tetraalkoxymethylolbenzguanamines and acetoguanamines e.g. tetramethoxymethylolbenzguanamine, tetrabutoxymethylolbenzguanamine and tetramethoxymethylol aceto-guanamine; and anhydrides and chlorides of such acids.

We have obtained good results by using as the surface active agent anionic surface active agents of poly(oxyethylene) type and anionic surface active agents. The non-ionic surface active agent of poly(oxyethylene) type includes: poly(oxyethylene) lauryl ether and like poly(oxyethylene) alkyl ethers



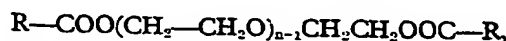
poly(oxyethylene) nonylphenyl ether and like poly(oxyethylene) alkylaryl ethers



poly(oxyethylene) oleate and like poly(oxyethylene) alkyl esters



or



poly(oxyethylene) stearylamine and like poly(oxyethylene) alkylamines



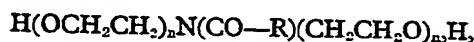
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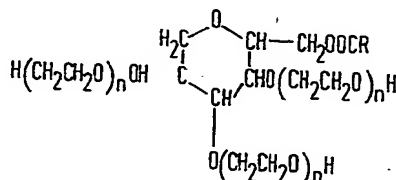
poly(oxyethylene) laurylamide and like poly(oxyethylene) alkylamides



or



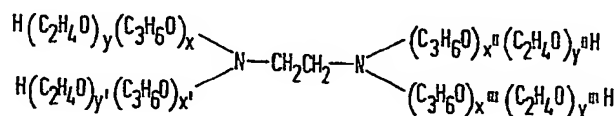
poly(oxyethylene)sorbitane monolaurate and like poly(oxyethylene)-sorbitane fatty acid esters



wherein, in the above formulae, R is an alkyl group containing 6 to 25 carbon atoms and n and n' are integers of 5 to 50, poly(oxyethylene) (oxypropylene) copolymers of Pluronic type



wherein a , b and c are integers greater than 1 and $(a+b+c)$ is 20 to 300, and of Tetronics type



wherein x to x''' and y to y''' are integers of greater than 1 and the sum of x to y''' is 20 to 600 (Pluronic in a Registered Trade Mark).

Examples of the anionic surface active agents are: alkylmethyltaurites, alkylbenzene sulfonates and alkylsulfates.

The coating composition thus obtained is, if necessary, mixed with 0.001 to 20, preferably 0.01 to 10% by weight, based on the weight of polymer, of a catalyst, such as trifluoroacetic acid, paratoluenesulfonic acid, triethylenediamine, aluminium chloride, tin chloride or hydrochloric acid and then applied, as shown in Fig. 2, to the surface 1 of an article, such as window-glass, automobile or aircraft windscreens, doors, mirrors, spectacle lenses, glass or plastics goggles or optical lenses, dried and cured at a temperature in the range of from 70 to 200°C for 5 minutes to 5 hours, preferably 15 minutes to 3 hours to form a coating film 2.

It is a preferred feature of the present invention that the cross-linking density decreases from the surface towards the interior of the resinous article.

For example a coating film, formed by a conventional coating, dipping or other suitable techniques may be treated by initiating and promoting a cross linking reaction from the surface of the resinous layer towards the interior. This may be achieved by e.g. infra red or ultra violet radiation or by momentarily heating the coated article

in an electric oven maintained at a high temperature. However, reproducibility of the results using these techniques is rather poor.

Preferably, in accordance with the invention a coating film or other article e.g. a contact lens or similar moulding is formed by coating or casting the hydrophilic hygroscopic resin incorporated with at most one of the crosslinking agent and catalyst; thereafter the article is exposed to a solution or vapour containing the other or both of the catalyst and cross-linking agent, as mentioned above. Thus one of the catalyst or cross-linking agent may initially be uniformly distributed through the resin; both these two components may, however, be incorporated into the resin by contacting the moulded resin article with a solution or vapour containing them both. The cross linking agent and/or the catalyst concentration will, accordingly decrease from the surface, towards the interior of the article, and hence, upon heat curing the degree of cross-linking will vary accordingly.

Thus, resinous coating films produced in accordance with the present invention may combine a good non-fogging property and a very high surface hardness while exerting a high resiliency in the vicinity of the surface of a substrate due to the cross-linking density gradient declining from the surface towards the interior of the coating film. It is believed that the resilient bottom portion of the coating film functions as an absorbing layer against stresses imposed to the surface to markedly enhance its abrasion resistance.

On the other hand, in the cases in which the catalyst or cross-linking agent has uniformly and sufficiently penetrated into the resinous layer there is obtained a uniformly cured resinous layer without a crosslinking density gradient. In these cases we have observed that not only is the hygroscopicity of the bottom portion impaired markedly but also the surface hardness may not be sufficient because of the lower stress absorbing capacity of the bottom portion.

Accordingly, in order to obtain a crosslinking density gradient suitable conditions of contact between the hygroscopic resinous layer with the solution or vapour containing the ingredients to be penetrated into the resinous layer have to be chosen appropriate for the particular combination of resinous layer and solution or vapour. For instance, a layer of a hygroscopic resin, 2-hydroxyethyl methacrylate polymer, coated on a glass sheet was, after being left in air for 30 minutes, soaked at 25°C for 1 or 10 minutes in an ethylene glycol monomethyl ether solution containing 0.5% by weight of hexamethoxy-methylolmelamine as crosslinking agent and 0.02% by weight of trifluoroacetic acid as catalyst and cured at 150°C for 30 minutes: cured film from the raw film soaked for 1 minute had excellent hygroscopicity and surface hardness while the cured film from the raw film soaked for 10 minutes had poor hygroscopicity and an unsatisfactory surface hardness.

However, it is essential that both the crosslinking agent and catalyst are present also in the deepest part of the final product, i.e. in the vicinity of a glass surface in case where a coating in applied to a glass surface, even though in slight amounts. For attaining this, a coating film is kept in contact with a solution or vapour containing a crosslinking agent and/or a catalyst until slight amounts of both reach there or both are previously incorporated in slight amounts in the coating resin.

The concentration of crosslinking agent may be, in case of solution, usually 0.01 to 20, preferably 0.1 to 5% by weight and, in case of vapour, usually 1 to 100, preferably 10 to 80% by volume. The concentration of catalyst may be, in case of solution usually 0.01 to 5, preferably 0.05 to 2% by weight and, in case of vapour, usually 0.1 to 50, preferably 1 to 20% by volume. The contact time, though varying depending on the temperature, may be, in case of solution, usually 1 second to 5 minutes, preferably 5 seconds to 1 minute and, in case of vapour, usually 1 second to 10 minutes, preferably 5 seconds to 3 minutes.

In addition, the pot life of a hygroscopic resin solution used in the present invention may be prolonged to a great extent. For instance, a hygroscopic resin solution is usually mixed with a cross-linking agent and/or a catalyst prior to application to substrates and, in this case, the pot life of the solution is usually 3 or 4 days and at most 1 week even if stored in a dark cool place and used in a well conditioned atmosphere. Contrary to this, in the practice of the method of present invention, the resin solution may be stored 3 months or more without any deterioration if the resin solution is stored separately from the crosslinking agent and catalyst.

Heat curing is usually carried out at 60 to 230, preferably 80 to 170°C for 5 minutes to 5 hours, preferably 30 minutes to 2 hours.

The present invention will be illustrated with respect to other embodiments thereof.

We have also observed that by subjecting a hygroscopic coating film having two

opposing properties, hygroscopicity and surface hardness, to a special treatment, both the properties are successfully enhanced.

When a hygroscopic resin contains only small amounts of a crosslinking agent, there is a relationship as shown in Fig. 6 between the amount of crosslinking agent and the non-fogging property of the hygroscopic resin. In the Figure, the number on the abscissa indicates the % chemical equivalent based on the equivalent weight of —OH groups contained in the hygroscopic resin and, since the reaction between the resin and crosslinking agent is believed to be through the functional groups in the crosslinking agent and the functional groups, i.e. —OH groups, in the resin, it is expected that there is a linear relationship between the absolute moisture regain of the resin and the amount of added crosslinking agent if all the functional groups in the crosslinking agent react with the functional groups in the resin.

The ordinate represents as the non-fogging capacity per unit thickness the values obtained by forming a non-fogging coating film on a surface of a 3 mm. thick sheet of glass and exposing the coated surface to a steam chamber while contacting the back surface with cooling water to determine the time until the non-fogging effect of the coating film disappears as indicated by development of water droplets on the coated surface and dividing the time by the thickness (3 to 30 microns) of the coating film. In the figure, the non-fogging capacities vs the amount added of a crosslinking agent, determined by fixing the temperature of steam at 39°C in the steam chamber and setting the temperature of the cooling water at 25°, 30° and 35°C, are plotted as curves A, B and C, respectively, and straight line D is an imaginary non-fogging capacity decay curve calculated on the basis of a reduction of the number of —OH groups in the resin through reaction with the crosslinking agent. It has been observed that the tendency as shown in the figure varies little with the kind of resin, crosslinking agent, substrate, curing conditions and other factors but is dependent on the change in properties the coating film itself created by the addition of varying amounts of crosslinking agent. The sudden decrease in non-fogging capacity over the decrease in concentration of the hydrophilic —OH groups in the hygroscopic resin caused by addition of the crosslinking agent is presumed to be attributable to the accelerative decrease in moisture absorbing rate on the surface and in the inside of the film caused by establishment of equilibrium between the quantity of water vapor reaching the surface of the film and the moisture absorbing rate on the surface and in the inside of the film. Accordingly, it is believed that the non-fogging capacity of a coating film is not so reduced so long as moisture is easily movable within the film even if the resinous coating film has been hardened by incorporation of a large amount of a crosslinking agent.

In a preferred embodiment the film is contacted with moisture during, before and/or after curing.

The contacting of the coating film with moisture may be attained by soaking it with its substrate in cold or warm water, optionally, controlling the contact therebetween by, e.g., irradiation of ultrasonic vibrations. Alternately, it may be attained by contacting the coating film with steam and there may be adopted any other suitable means. For instance, a marked improvement in non-fogging capacity is attained within 1 day when a coating film is exposed to steam at temperatures above 90°C, it needs 1 to 2 days at 70 to 80°C and 6 to 7 days at 40°C, but at temperatures below 30°C there is obtained little improvement. On the other hand, when a crosslinked coating film is soaked in water at room temperature a treatment by ultrasonic waves for 2 to 3 minutes is usually found to be sufficient and at 50°C the treatment for 1 to 2 minutes is usually sufficient. A satisfactory result is obtainable by contacting the coating film with superheated steam at 150°C for 30 minutes to effect crosslinking concurrently with moisture contact.

While the true reason or exact mechanism for such improvement in non-fogging capacity of a hygroscopic coating film brought about by the method of the present invention is uncertain, it is believed that when a hygroscopic resinous coating film is subjected to a crosslinking reaction after contact with moisture there are present in the film an organic solvent and water; during the curing step, first the low boiling organic solvent volatilizes from the coating film and then the high boiling water causes interaction with advancement of the crosslinking reaction; the vapourizing water causes interaction between water molecules and the hygroscopic functional groups, e.g. hydroxyl groups, contained in the polymer molecules constituting the hygroscopic resin so as to arrange the hydroxyl groups on the surface of the film. Thus, after completion of crosslinking reaction, numerous hydrophilic —OH groups capable of fastening moisture are arranged in the surface of the coating film and, consequently, enhance the non-

fogging capacity of the film. On the other hand, it also is believed that, when a coating film is contacted with moisture after crosslinking, a large quantity of moisture is introduced into the interior of the coating film and the repeated penetration and exhaustion of water molecules into and out of the inside of the coating film makes the mobility of water molecules in the coating film sufficiently high as to increase the moisture absorbing rate of the coating film and, consequently, enhance its non-fogging capacity. In the case where a coating film is subjected to contact with moisture during curing, both effects can be achieved. Developing this idea, it is to be expected that a similar result could be obtained by use of a polar solvent in place of water and, after many investigations using various alcohols as well as water; we have found that water gives the best result and alcohols give a fairly good result.

The contacting of a resinous coating film with moisture can be carried out using any process as mentioned above, e.g. by soaking in or exposing to cold or warm water or steam or otherwise contacting, optionally, accelerating the contact by means of, e.g. ultrasonic waves. When a coating film is soaked in cold or warm water, there occasionally remain water drops on the surface of the coating film because of the difference in surface tension between water and the coating film and this results in a rough, unsightly surface. This may conveniently be avoided by adding a trace of a surface active agent to the cold or warm water, usually in amounts of 0.001 to 2% by weight, preferably of 0.01 to 0.5% by weight.

The surface active agent added to the water may be any of the nonionic, cationic, anionic and amphoteric surface active agents. Suitable nonionic surface active agents include: poly(oxyethylene) alkyl ethers, poly(oxyethylene) alkylaryl ethers, poly(oxyethylene) alkanolates, poly(oxyethylene) alkanamides, poly(oxyethylene) sorbitane, alkanolates, Pluronics and Tetronics; the anionic surface active agents include alkyl methyltaurites, alkylbenzenesulfonates, alkylsulfates and likes, and the cationic surface active agent includes higher fatty acid amine salts and quaternary ammonium salts.

Average molecular weight of the resin used in the present invention is suitably 5,000 to 1,000,000, preferably 30,000 to 200,000. The average molecular weight may be determined by using light scattering method measuring intrinsic viscosity $[\eta]$ in dimethyl formamide solution at a temperature of 25°C and calculating based on the following formula:

$$[\eta] = A M^{\alpha}$$

wherein $[\eta]$ is intrinsic viscosity, α is a constant ($=8.9 \times 10^{-5}$) and A is a constant ($=0.72$). In the following Examples, the average molecular weights are determined by the above described light scattering method.

In the following Examples, all parts and percentages are by weight unless otherwise designated.

Example 1

An 18% ethylene glycol mono-methyl ether solution of a 2-hydroxyethyl methacrylate prepolymer having about 40,000 of average molecular weight, sold under the Registered Trade Mark "Hydron", was employed as a hygroscopic resin base and mixed with 15% chemical equivalent, based on the resin solid, of trimellitic acid and 15%, based on the resin solid, of poly(oxyethylene) nonylphenyl ether, sold under trade name "Emulgen 950" by Kao-Atlas Co., Ltd., as a surface active agent. The composition was mixed with 1.0% of p-toluenesulfonic acid based on the resin solid as a catalyst and applied to a 100 mm × 100 mm × 3 mm polycarbonate sheet, left in air for 30 minutes to evaporate the solvent and then hot cured at 130°C for 40 minutes to form a 10 microns thick hygroscopic resinous coating layer. A specimen A of the coating film and a specimen B of the same polycarbonate sheet uncoated were subjected to the abrasion test. Noticeable scratches were formed on specimen A in 45 minutes, and on specimen B in 5 minutes. When expiration was directed to the specimen A and B, the latter was densely fogged and became opaque while the surface of the specimen A was not fogged at all.

Example 2

A 2-hydroxyethyl methacrylate prepolymer having about 40,000 of average molecular weight as a hygroscopic resin base was mixed with 10% chemical equivalent, based on the resin solid, of a partially methylated hexamethylolmelamine (sold under the Registered Trade Mark "Uformite") and 5%, based on the resin solid, of an alkyl methyltaurite (trade name "Liphoran L", sold by Lion Oils & Fats Co.) as a surface active agent, and then with 0.5% of trifluoroacetic acid based on the resin solid as a catalyst. The resinous coating was applied to a 100 mm × 100 mm × 3 mm poly(methyl methacrylate) sheet, dried and subjected to curing at 100°C for 30

minutes to form thereon an hygroscopic resin layer approximately 8 microns thick, specimen C.

Another coating film of the same thickness, specimen D, was formed in the same procedure except of use of hexamethoxymethylol melamine (trade name "Cymehl 303") in place of the Uformite as used in the preparation of the specimen C.

Yet another coating film of the same thickness was formed by the same procedure except that pyromellitic anhydride of first reagent grade was used in place of Cymehl 303 and employed a curing temperature of 130°C, specimen E, because of the somewhat lower reactivity of the pyromellitic anhydride compared with those of the other two crosslinking agents.

The three specimens and specimen F of the uncoated substrate acrylate sheet were subjected to the same performance test as in Example 1 to obtain the results as summarized in the following Table 1.

TABLE 1

Specimen	Abrasion Test	Expiration Test
C	Slightly damaged in 30 minutes	Fogged after short period
D	Slightly damaged in 40 minutes	Not fogged at all
E	Slightly damaged in 60 minutes	Not fogged at all
F	Markedly damaged in 1 minute	Completely fogged

As indicated by the above Table 1, the specimen C is somewhat inferior in non-fogging property because of use of Uformite having a self-condensing property, and in hardness to specimens D and E presumably because of the plasticizing effect of the product resulting from the self-condensation of the crosslinking agent, while, on the other hand, the specimen D and E have excellent in non-fogging characteristics because of the inherent non-selfcondensing property of the crosslinking agents used in their preparation. The superiority in abrasion resistance of specimens E and D is believed to be attributable to the lower swellability of specimen E than specimen D upon the expiration test because, in specimen E, the benzene skeleton is separated from the crosslinking point by two atoms, i.e. an oxygen atom and a carbon atom, while, in the specimen D, the triazine skeleton is separated from the crosslinking point by 3 atoms, i.e. an oxygen atom, a carbon atom and a nitrogen atom.

Example 3

A 50 mm×50 mm×3 mm sheet glass 1 was coated, as illustrated in Fig. 3, with an 18% ethylene glycol monomethyl ether solution of a hygroscopic resin, poly(2-hydroxyethyl methacrylate) having about 40,000 average molecular weight, mixed with 5%, based on the solid resin, of hexamethoxymethylolmelamine and 10% of polyoxyethyleneglycol ester of a fatty acid (trade name: Emanone, Kao Atlas Co., Ltd.) based on resin solid to form a resinous layer 2. The resinous coating layer was, after being dried at 25°C for 30 minutes to evaporate the solvent, exposed for 10 seconds to a vapor of trifluoroacetic acid as a catalyst, as illustrated in Fig. 4 wherein numeral 3 indicates a deposited layer of the catalyst and 4 indicates a region in which catalyst has diffused and penetrated into the resinous layer 2 of the catalyst. After being left in air at 25°C for 30 minutes, the coating film on the sheet glass was heated at 130°C for 40 minutes in an electric oven to obtain a non-fogging coating film in a curing state as schematically shown in Fig. 5 wherein numeral 5 indicates the variable crosslinking density gradually decreasing from the surface toward the substrate.

Specimen H having a cross-section as shown in Fig. 3 was prepared by using an ethylene glycol monomethyl ether solution of a 2-hydroxyethyl methacrylate prepolymer mixed with 5% of hexamethoxymethylolmelamine and 10% of polyoxyethyleneglycol ester of a fatty acid (trade name: Emanone, Kao Atlas Co., Ltd.) based on resin solid, further 0.1% of trifluoroacetic acid as a catalyst, each % being based on the resin solid; applying the composition to a sheet glass and curing the resulting coating film under the same curing conditions as were used to prepare specimen G. The specimens were subjected to determination of non-fogging property and surface hardness. The thickness of the coating film was about 8.5 microns in both the specimen G and H.

The non-fogging property of the specimens was determined as follows: after having washed both specimens sufficiently with water, the coating film was exposed to water vapor at 37°C while chilling the reverse side of the sheet glass to 25°C by means of recirculating water; the time needed for the development of fogs was noted; the specimens were thereafter placed in a cold store at -15°C for 10 minutes, then

left in a room maintained at 25°C, 65% RH, and the time needed for disappearance of the fogs was noted.

The surface hardness was determined by a test method in accordance with Japanese Industrial Standard (JIS) T 8147, i.e. a fall-sand test in which 500 g of emery sand of 80 mesh size was dropped from a height of 62 cm onto the surface of the coating film and the film was then subjected to haze reading by means of a haze meter. Other examples of specimens G and H were subjected to the rotary abrasion test using a rotary disc having a diameter of 30 mm. The specimens were rotated on a turn table at 120 r.p.m. under a load of 1 Kg/cm² imposed thereto through a doubled gauze layed thereover. The time taken for the abrasion to impair the transparency of the film by scratches was noted. The results of the above 4 tests were as summarized in the following Table 2.

TABLE 2

Specimen	Non-fogging property		Surface hardness	
	Time till fogged	Time till defogged	Fall-sand haze	Abrasion test
G	28 sec.	6 mins.	14.5%	70 mins.
H	32 sec.	7 mins.	32.0%	5 mins.

Example 4

An 18% solution in ethylene glycol monomethyl ether of 2-hydroxyethyl methacrylate-methyl methacrylate (95:5 molar ratio) copolymer having about 40,000 average molecular weight incorporated with 8%, based on the resin solid, of pyromellitic anhydride and 2% of dialkylsulfosuccinate (trade name: Lipal SA, Lion Yushi Kabushiki Kaisha based on the resin solid as an anionic surface active agent was applied to a 50 mm×50 mm×3 mm sheet glass and dried at 100°C for 5 minutes for elimination of solvent. The glass sheet was then soaked for 30 seconds in a 0.2% hydrochloric acid solution in ethylene glycol monomethyl ether, then dried in air for 30 minutes and subjected to curing at 140°C for 30 minutes in an electric oven to obtain a specimen I.

On the other hand, the same coating solution, except that it was further mixed with 0.05%, based on the resin solid, of hydrochloric acid was applied to a glass sheet of the same dimensions and subjected to drying and curing under the same conditions without treatment in the catalyst solution to obtain specimen J.

The specimen I and J thus prepared, both being a thickness of 9.2 microns, were subjected to non-fogging property and surface hardness determinations to obtain the results as summarized in the following Table 3.

TABLE 3

Specimen	Non-fogging property		Surface hardness	
	Time till fogged	Time till defogged	Fall-sand haze	Abrasion test
I	33 sec.	6.5 mins.	13.2%	80 mins.
J	36 sec.	8 mins.	34.0%	5 mins.

WHAT WE CLAIM IS:—

1. A resinous coating composition forming a hygroscopic non-fogging coating film having a high surface hardness comprising a hygroscopic resin which is a polymer or co-polymer of at least one hydrophilic monomer chosen from hydroxy-lower alkyl acrylates, hydroxy-lower alkyl methacrylates, hydroxy-lower alkoxy lower alkyl acrylates and hydroxy lower alkoxy-lower alkyl methacrylates incorporated with (a) 5 to 60% by weight, based on resin solid, of a surface active agent chosen from nonionic surface active agents of the polyoxyethylene type and anionic surface active agents and (b) 5 to 70 equivalent %, based on resin solid, of a crosslinking agent in which at least 80% of the functional groups are of the same kind and having a single- or condensed- ring carbo- or heterocyclic skeleton, each ring being a 4- to 8-membered ring and the number of atoms forming the straight chain linkage between said skeleton and the reaction point of the hygroscopic resin with the crosslinking agent being at most 4 inclusive of the atom on said resin at the reaction point.

2. A composition according to Claim 1, in which the surface active agent is incorporated in an amount of 15 to 40% by weight, based on the weight of the hygroscopic resin solid.

3. A composition according to Claim 1 or Claim 2, in which the crosslinking agent is incorporated in an amount of 15 to 40% by equivalent weight based on the equivalent weight of the hygroscopic resin solid.

4. A composition according to anyone of Claims 1 to 3, in which the hygroscopic resin is a polymer or copolymer of at least one monomer chosen from 2-hydroxy-ethyl acrylate and 2-hydroxy-methacrylate.

5. A composition according to anyone of Claims 1 to 4, in which the cyclic skeleton of the crosslinking agent is a benzene ring, naphthalene ring, triazine ring, pyridine ring, quinoline ring, isoquinoline ring or imidazole ring.

6. A composition according to anyone of Claims 1 to 5, in which the crosslinking agent is an aromatic polycarboxylic acid or its anhydride or chloride.

7. A composition according to anyone of Claims 1 to 5, in which the crosslinking agent is chosen from hexaalkoxymethylol-melamines, and tetraalkoxymethylol-benzoguanamines and -acetoguanamines.

8. A resin composition, substantially as hereindescribed with reference to anyone of the Examples.

9. A method of coating a substrate with a hygroscopic non-fogging resin having a high surface hardness comprising coating the substrate with a film of a resinous coating composition as defined in anyone of Claims 1 to 7 and then curing said film.

10. A method according to Claim 9, in which the film is contacted with moisture, during, before and/or after curing.

11. A method according to Claim 10, in which the moisture contains 0.001 to 2% by weight of surface active agent.

12. A method according to Claim 10 or 11, in which the hygroscopic resin contains 0.001 to 20% by weight of a catalyst.

13. A method of coating an article with a hygroscopic non-fogging resin having a high surface hardness substantially as herein described, with reference to anyone of the Examples.

14. An article having a high surface hardness comprising a substrate having thereon a cured coating film formed from a hygroscopic resinous composition as defined in anyone of Claims 1 to 7.

15. An article coated with a cured coating film formed from a hygroscopic resinous composition, substantially as hereindescribed with reference to anyone of the Examples.

16. A method of making a hygroscopic hydrophilic resinous article having a high surface hardness, which comprises:

a) moulding a hygroscopic resin to a desired shape; the resin being a polymer or co-polymer of at least one hydrophilic monomer chosen from hydroxy-lower alkyl acrylates, hydroxy-lower alkyl methacrylates, hydroxy-lower alkoxy lower alkyl acrylates and hydroxy-lower alkoxy-lower alkyl methacrylates incorporated with (i) 5 to 60% by weight, based on resin solid of a surface active agent chosen from non ionic surface active agents and possibly (ii) one component chosen from a catalyst and a cross linking agent as defined in Claim 1;

b) contacting the surface of the moulded article with a solution or vapour containing both, or the other of, the catalyst and cross-linking agent until it or they penetrate into the article and has or have a concentration therein gradually decreasing from the surface of the article towards the interior; at least the surface of the article resulting from operation (b) containing cross-linking agent in an amount of 5 to 70% equivalent based on the resin solid; and

c) then heat curing the article

17. A method according to Claim 16 in which the cross-linking agent is incorporated in the resin to be moulded in an amount of 5 to 70 equivalent % based on the resin solid.

18. A method according to Claim 16 or 17, in which the moulded article is contacted with a solution containing 0.01 to 5% by weight of the catalyst.

19. A method according to Claim 16 or 17, in which the moulded article is contacted with a vapour containing 0.1 to 50% by volume of catalyst.

20. A method according to Claim 16 in which the catalyst is incorporated into the resin in an amount of 0.001 to 20% by weight based on the weight of polymer.

21. A method according to Claim 16 or 20, in which the moulded article is contacted with a solution containing 0.01 to 20% by weight of cross-linking agent.

22. A method according to Claim 16 or 20 in which the moulded article is contacted with a vapour containing 1 to 100% by volume of cross-linking agent.

23. A method according to anyone of Claims 16, 17, 18, 20 or 21 in which the moulded article is contacted with the solution for a period ranging from 1 second to 5 minutes.

24. A method according to anyone of Claims 16, 17, 19 or 22 in which the

moulded article is contacted with the vapour for a period ranging from 1 second to 10 minutes.

25. A method according to anyone of Claims 16 to 24, in which the catalyst is at least one compound chosen from trifluoro-acetic acid, p-toluene sulfonic acid, tri-ethylene diamine, aluminium chloride, tin chloride and hydrochloric acid.

26. a hygroscopic resinous article produced by the method of anyone of Claims 16 to 25.

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COMPLETE SPECIFICATION

2 SHEETS

*This drawing is a reproduction of
the Original on a reduced scale
Sheet 1*

FIG. 1

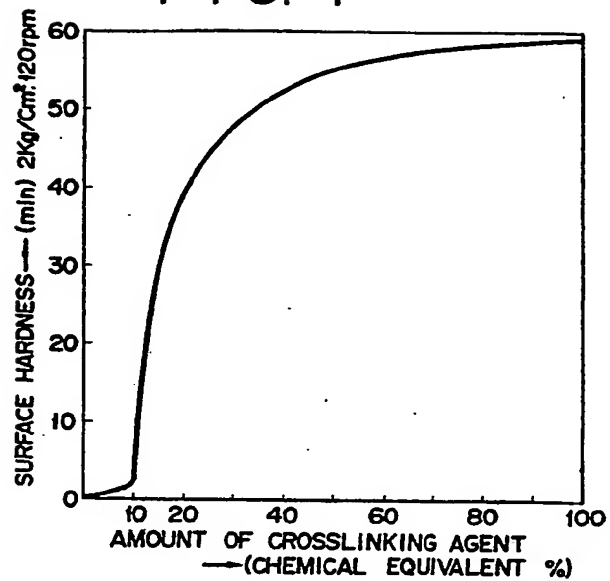


FIG. 2



FIG. 3



FIG. 4

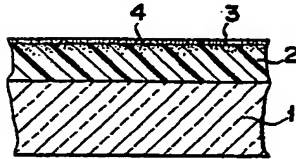


FIG. 5

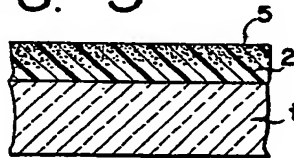


FIG. 6

